## UNITED STATES PATENT AND TRADEMARK OFFICE **CERTIFICATE OF CORRECTION**

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Page 1 of 18

APPLICATION NO.: 09/885609

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INVENTOR(S)

: Mak et al.

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Please delete entire patent title pages, drawings 1-6, and columns 1 line 1 and columns 10 line 32

And insert title pages, drawings 1-6, and columns 1 line 1 and columns 10 line 32 as shown on the attached pages.

Signed and Sealed this

Sixth Day of May, 2008

JON W. DUDAS Director of the United States Patent and Trademark Office

## (12) United States Patent Mak et al.

(54) SYSTEM AND METHOD TO FORM A

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		TIAL DEPOSITION TECHNIQUES
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(51)	Int. CL7	71 \$#4 2 <b>4</b> \$ 4 <b>\$</b> 2 <b>4</b> 2 <b>4</b> 2 <b>4</b> 3	HOLL 21/44
	U.S. Cl.	*****	. <b>438/679; 438/</b> 769; 438 <i>/</i> 775; ; 438/683; 438/682; 257 <i>/</i> 751; 427/255.2
(59)	Elala of	Cananh	A18/670 627

#### (56)References Cited

U.S.	PATENT	DOCUMENT

438/644, 654, 682, 683, 685, 769, 770, 775

4,058,430 A	11/1977	Suntols et al.
4,389,973 A	6/1983	Suntola et al.
4,413,022 A	11/1983	Suntoia et al.
4,486,487 A	12/1984	Skarp 429/216
4,767,494 A	8/1988	Kobayashi et al.
4,806,321 A	2/1989	Nishizawa et al.
4,813,846 A	3/1989	Helms 414/744.1
4,829,022 A	5/1989	Kobayashi et al 437/107
4,834,831 A	5/1989	Nishizawa et al 156/611
4,838,983 A	6/1989	Schumaker et al 156/613
4,838,993 A		Aoki et al 156/643

4,840,921 A	6/1989	Matsumoto
4.845.049 A	7/1989	Sunakawa
4.859.625 A	8/1989	Nishizawa et al 437/81
4.859.627 A	8/1989	Snnakawa
4.861.417 A	8/1989	Mochizuki et al.
4.876.218 A	10/1989	Pessa et al.
4,917,556 A	4/1990	Stark et al 414/217
4.927.670 A	5/1990	Erbil 427/255.3
4.931,132 A	6/1990	Aspnes et al 156/601
4,951,601 A		Maydan et al 118/719
4,960,720 A		Shimbo 437/105
4.975.252 A	12/1990	Nishizawa et al 422/245
4,993,357 A	2/1991	Scholz

#### (List continued on next page.)

### FOREIGN PATENT DOCUMENTS

DE	196 27 017	1/1997
DE	198 20 147	7/1999
EP	0 344 352 A1	12/1989

(List continued on next page.)

### OTHER PUBLICATIONS

Rossnagel, et al. "Plasma-enhanced Atomic Layer Deposition of Ta and Ti for Interconnect Diffusion Barriers," J. Vacuum Sci. & Tech. B., vol. 18, No. 4 (Jul. 2000), pp. 2016-2020.

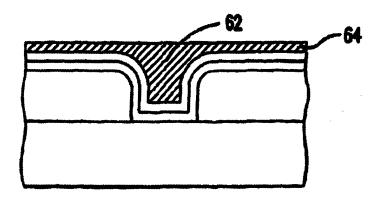
(List continued on next page.)

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### **ABSTRACT**

A system and method to form a stacked barrier layer for copper contacts formed on a substrate. The substrate is serially exposed to first and second reactive gases to form an adhesion layer. Then, the adhesion layer is scrially exposed to third and fourth reactive gases to form a barrier layer adjacent to the adhesion layer. This is followed by deposition of a copper layer adjacent to the barrier layer.

### 49 Claims, 6 Drawing Sheets



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17.0	D-277723	DAGEN FOLING	4 747 117 4	FARRE	75
U.S.	. PATENI	DOCUMENTS	5,747,113 A		Trai
5,000,113 A	3/1991	Wang et al 118/723	5,749,974 A 5,788,447 A		Yonemitsu et al 414/217
5,013,683 A	5/1991	Petroff et al 437/110	5,788,799 A		Steger et al 156/345
5,028,565 A		Chang et al 437/192	5,796,116 A		Nakata et al
5,082,798 A		Arimoto	5,801,634 A		Young et al 340/635
5,085,885 A		Foley et al 477/38	5,804,488 A		Shih et al.
5,091,320 A 5,130,269 A		Aspnes et al	5,807,792 A	9/1998	lig et al 438/758
5,166,092 A		Mochizuki et al.	5,830,270 A		McKee et al 117/106
5,173,474 A		Connell et al 505/1	5,835,677 A	11/1998	Li et al 392/401
5,186,718 A		Tepman et al 29/25.01	5,851,849 A		Comizzoli et al.
5,205,077 A		Wittstock 51/165 R	5,855,675 A		Doering et al 118/719
5,225,366 A		Yoder	5,855,680 A		Soinings et al.
5,234,561 A 5,246,536 A		Randhawa et al 204/192.38 Nishizawa et al 156/610	5,856,219 A 5,858,102 A		Naito et al
5,250,148 A		Nishizawa et al.	5,866,213 A		Poster et al 427/573
5,254,207 A		Nishizawa et al 156/601	5,866,795 A		Wang et al.
5,256,244 A		Ackerman	5,879,459 A		Gadgil et al.
5,259,881 A		Edwards et al 118/719	5,882,165 A		Maydan et al 414/217
5,270,247 A		Sakuma et al.	5,882,413 A		Besulieu et al 118/719
5,278,435 A 5,281,274 A	1/1994	Van Hove et al.	5,904,565 A		Nguyen et al 438/687
5,286,296 A		Sato et al 118/719	5,916,365 A 5,923,056 A		Sherman Lee et al
5,290,748 A		Knuuttila et al.	5,923,985 A		Aoki et al
5,294,286 A		Nishizawa et al.	5,925,574 A		Aoki et al
5,296,403 A		Nishizawa et al 437/133	5,928,389 A	7/1999	Jevtic 29/25.01
5,300,186 A		Kitahara et al.	5,942,040 A		Kim et al 118/726
5,306,666 A		Izomi 437/192	5,942,799 A		Danek et al 257/751
5,311,055 A 5,316,615 A		Goodman et al 257/593	5,947,710 A		Cooper et al
5,316,793 A		Copel	5,972,179 A 5,972,430 A		Chittipeddi et al 204/192.17 DiMeo, Jr. et al 427/255.32
5,330,610 A		Eres et al.	5,989,623 A		Chen et al 427/97
5,336,324 A	8/1994	Stall et al.	6,001,669 A		Gaines et al 438/102
5,338,389 A		Nishizawa et al.	6,015,590 A		Suntola et al.
5,348,911 A	9/1994	Jurgensen et al 117/91	6,025,627 A		Forbes et al.
5,374,570 A 5,393,565 A		Name et al.	6,036,773 A		Wang et al.
5,395,791 A		Suzuki et al	6,042,652 A 6,043,177 A		Hyun et al
5,438,952 A		Otsuka 117/84	6,051,286 A		Zhao et al
5,439,876 A		Graf et al 505/447	6,062,798 A		Muka
5,441,703 A		Jurgensen 422/129	6,071,808 A		Merchant et al.
5,443,033 A		Nishizawa et al.	6,084,302 A		Sandhu
5,443,647 A 5,455,072 A		Aucoin et al.	6,086,677 A		Umotoy et al 118/715
5,458,084 A		Bension et al 427/255.7 Thorae et al.	6,110,556 A 6,113,977 A		Bang et al 428/64.1 Soinings et al.
5,469,806 A		Mochizuki et al	6,117,244 A		Bang et al 118/715
5,480,818 A		Matsumoto et al.	6,124,158 A		Dautartas et al.
5,483,919 A		Yokoyama et al.	6,130,147 A	10/2000	Major et al.
5,484,664 A		Kitahara et al.	6,139,700 A		Kang et al 204/192.17
5,503,875 A		Imai et al	6,140,237 A		Chan et al.
5,521,126 A 5,526,244 A		Okamura et al 437/235 Bishop 362/147	6,140,238 A	10/2000	Learn
5,527,733 A		Nishizawa et al 437/160	6,143,659 A 6,144,060 A	11/2000	
5,532,511 A		Nishizawa et al.	6,158,446 A		Mohindra et al 134/25.4
5,540,783 A		Eres et al 118/725	6,174,377 B1	1/2001	Doering et al 118/729
5,580,380 A		Liu et al.	6,174,809 B1	1/2001	Kang et al 438/682
5,601,651 A		Watabe 118/715	6,183,563 B1	2/2001	Choi et al 118/715
5,609,689 A		Kato et al	6,197,683 B1		Kang et al 438/643
5,616,181 A 5,637,530 A	6/1997	Yamamoto et al 118/723 ER Gaines et al.	6,200,893 B1	3/2001	
5,641,984 A	6/1997	Aftergut et al 257/433	6,203,613 B1 6,206,967 B1		Gates et al
5,644,128 A	7/1997	Wollnik et al 250/251	6,207,302 B1		Sugiura et al 428/690
5,667,592 A	9/1997	Boitnott et al 118/719	6,207,487 B1		Kim et al 438/238
5,674,786 A	10/1997	Turner et al 437/225	6,218,298 B1	4/2001	
5,693,139 A		Nishizawa et al.	6,231,672 B1		Choi et al 118/715
5,695,564 A 5,705,224 A		Imahashi 118/719	6,248,605 B1		Harkonen et al 438/29
5,707,880 A		Murota et al. Aftergut et al	6,270,572 BI 6,271,148 B1		Kim et al
5,711,811 A		Suntols et al.	6,284,646 B1		Leem
5,730,801 A		Tepman et al 118/719	6,287,965 B1		Kang et al 438/648
5,730,802 A		Ishizumi et al.	6,291,876 B1		Stumborg et al 257/632

# US 6,849,545 B2 Page 3

6,305,314	Bl	10/2001	Sneh et al 118/723 R	2002/005523	5 A1	5/2002	Agarwal et al 438/430
6,306,216	BI	10/2001	Kim et al 118/725	2002/0061613	2 A1		Sandbu et al 438/151
6,316,098	BI	11/2001	Yitzchaik et al 428/339	2002/007458			Lee
6,333,260	BI	12/2001	Kwon et al 438/643	2002/007650			Chiang et al 427/569
6,335,280			van der Jeugd	2002/007683			Hujanen et al
6,342,277			Sherman 427/562	2002/008184			Park et al
6,348,376			Lim et al 438/253	2002/008611			Byun et al.
6,355,561			Sandhu et al 438/676	2002/008650			Park et al 438/585
6,358,829			Yoon et al 438/597	2002/0090829			Sandhu 438/761
6,368,954			Lopatin et al 438/627	2002/009247		7/2002	Kang et al 118/715
6,369,430			Adetuta et al 257/382	2002/0094689	) A1		Park 438/694
6,372,598 6,391,785			Kang et al	2002/010508			Yang et al 257/774
6,399,491			Jeon et al	2002/010653			Lee et al 428/702
6,416,577			Suntoloa et al	2002/010684			Seutter et al
6,420,189			Lopatin 438/2	2002/010916			Kim et al
6,423,619			Grant et al 438/589	2002/011739			Chen et al
6,432,821	Bl		Dubin et al 438/678	2002/012124			Nguyen et al.
6,447,607			Soininen et al 117/200	2002/012134			Nguyen et al.
6,447,933			Wang et al 428/635	2002/012169	7 A1	9/2002	Marsh 257/751
6,451,119 6,451,695			Sneh et al 118/715	2002/013430			Choi 118/715
6,455,421			Sneh	2002/013507			Kang et al 257/767
6,458,701			Chae et al	2002/015572			Salla et al
6,468,924			Lee et al 438/763	2002/0162500 2002/0177282			Sneh et al
6,475,276	BI	11/2002	Elers et al 117/84	2002/0182320			Leskala et al 427/250
6,475,910	BI	11/2002	Sneh 438/685	2002/0187250			Elers et al
6,478,872			Chac et al 117/88	2002/018763			Kim et al 438/637
6,481,945			Hasper et al 414/217	2002/019016			Hall et al 248/188.7
6,482,262			Elers et al 117/84	2003/0013300		1/2003	Byun
6,482,733 6,482,740			Rasijmakers et al 438/633 Soininen et al 438/686	2003/0013324			Kim et al 438/778
6,495,449			Nguyen 438/627	2003/003180			Elers et al
6,511,539			Raaijmakers et al 117/102	2003/0032281			Werkhoven et al 438/640
6,534,395			Werkhoven et al 438/627	2003/0049942 2003/0054631			Haukka et al 438/778 Rasjimskers et al.
6,548,424	B2		Putkonen 438/785	2003/0072975			Shero et al
6,551,929			Kori et al.	2003/0082300			Todd et al 427/255.27
6,599,572			Saanila et al.	2003/0089308	A1		Rasijmakers
6,607,976			Chen et al.	2003/0101927	A)	6/2003	Raajimakers
6,632,279 6,686,271			Ritala et al. Raaijmakers et al.	2003/0104126			Fang et al.
2001/0000866		5/2001		2003/0129826			Werkhoven et al.
2001/0002280			Sneh 427/255.28	2003/0134508			Rasjimakers et al.
2001/0009140	A1		Bondestam et al 118/725	2003/0143841			Rasjimakers et al. Yang et al.
2001/0009695	A1	7/2001	Saanila et al 427/255.39	2003/0165615			Asitonen et al.
2001/0011526			Doering et al 118/729	2003/0168750			Basceri et al.
2001/0013312			Soininen et al 117/86	2003/0173586	A1		Moriwaki et al.
2001/0014371 2001/0024387		8/2001 9/2001	Kilpi	2003/0186495			Saanila et al.
2001/0028924			Rasijmakers et al 365/200 Rasijmakers et al 365/200	2003/0205729	Al	11/2003	Basceri et al.
2001/0029094			Mee-young et al 438/597	77/	\D. 177.C	NT DAGGT	NE POCI II CENTRE
2001/0031562			Rasimakers et al 438/770	74	MBIU	IN PALE	NT DOCUMENTS
2001/0034123	Al	10/2001	Jeon et al 438/643	EP	0 429	270 A2	5/1991
2001/0041250			Werkhoven et al 428/212	EP		490 A1	8/1991
2001/0042523			Kesala 122/6.6	EP		2641	10/1997
2001/0050039			Park	EP	1 167		1/2002
2001/0054377 . 2001/0054730 .			Lindfors et al 117/104	FR 70	2 626		7/1989
2001/0054769			Kim et al 257/301 Rasijmakers et al 257/758	FR CIB	2 692 2 355		12/1993 5/2001
2002/0000196			Park	GB	2355		5/2001
2002/0000598			Kim et al	JP	58-098		6/1983
2002/0004293			Soinnen et al 438/584	JP	58-100		6/1983
2002/0007790 .			Park 118/715	JP .		5712 A	4/1985
2002/0019121			Pyo 438/618	JP .	61-035		2/1986
2002/0021544			Cho et al	JP	61-210		9/1986
2002/0031618			Sherman	JP	62-069		3/1987
2002/0037630 / 2002/0041931 /			Agarwai et al 438/430	ЛР 10		495 A	4/1987 4/1097
2002/0041931 / 2002/0048635 /			Suntofa et al 427/255.28 Rim et al	JP JP	62-141 62-167		6/1987 7/1987
2002/0048880			Lee	JP	62 171		7/1987
2002/0052097			Park	JР	62-232		10/1987

# US 6,849,545 B2 Page 4

JP	63-062313	3/1988	IP	04/151822	5/1992
JP	63-085098	4/1988	IP	04-162418	6/1992
JР	63-090833	4/1988	JP.	04-175299	6/1992
JP	63-222420	9/1988	JP	04-186824	7/1992
1b	63-222421	9/1988	JP	04-212411	8/1992
1b	63-227007	9/1988	IP.	04-260696	9/1992
JP	63-252420	10/1988	JP.	04-273120	9/1992
JP	63-266814	11/1988	JP	04-285167	10/1992
JP	64-009895	1/1989	IP	04-291916	10/1992
JP JP	64-009896 64-009897	1/1989	IP	04-325500 04-328874	11/1992 11/1992
JP	64-037832	1/1989 2/1989	JP JP	05-029228	2/1993
JP	64-082615	3/1989	л	05-047665	2/1993
JP	64-082617	3/1989	JP	05-047666	2/1993
JP	64-082671	3/1989	JP	05-047668	2/1993
JP	64-082676	3/1989	JP	05-074717	3/1993
ъ	01-103982	4/1989	JP	05-074724	3/1993
JP	01-103996	4/1989	<u>IP</u>	05-102189	4/1993
JP JP	64-090524 01-117017	4/1989 5/1989	JP JP	05-160152	6/1993 7/1993
л ЛР	01-143221	6/1989	JP JP	05-175143 05-175145	7/1993 7/1993
ĴР	01-143233	6/1989	ĴР	05-182906	7/1993
JP.	01-154511	6/1989	ÎP	05-186295	7/1993
JP	01-236657	9/1989	JP	05-206036	8/1993
JP	01-245512	9/1989	JP	05-234899	9/1993
JP JP	01-264218	10/1989	ДP	05-235047	9/1993
JP JP	01-270593 01-272108	10/1989 10/1989	IP IP	05-251339 05-270997	9/1993 10/1993
JP	01-290221	11/1989	JP	05-283336	10/1993
JP	01-290222	11/1989	ïР	05-291152	11/1993
JP	01-296673	11/1989	JP	05-304334	11/1993
JP	01-303770	12/1989	JP	05-343327	12/1993
1b	01-305894	12/1989	<u>IP</u>	05-343685	12/1993
JP JP	01-313927 02-012814	12/1989 1/1990	JP	06-045606	2/1994
JP	02-012514	1/1990	JP JP	06-132236 06-177381	5/1994 6/1994
JP	02-017634	1/1990	JP	06-196809	7/1994
JP	02-063115	3/1990	JP	06-222388	8/1994
JP	02-074029	3/1990	JP	06-224138	8/1994
JP	02-074587	3/1990	1P	06-230421	8/1994
JP JP	02-106822 02-129913	4/1990 5/1990	JP JP	06-252057	9/1994
JP	02-162717	6/1990	JP	06-291048 07-070752	10/1994 3/1995
JP	02-172895	7/1990	TP	07-086269	3/1995
JP	02-196092	8/1990	JP	08-181076	7/1996
JP	02-203517	8/1990	JP	08-245291	9/1996
JP	02-230690	9/1990	л	08-264530	10/1996
JP JP	02-230722 02-246161	9/1990	JP	09-260786	10/1997
ĴР	02-264491	10/1990 10/1990	JP IP	09-293681 10-188840	11/1997 7/1998
JР	02-283084	11/1990	JP	10-190128	7/1998
JP	02-304916	12/1990	JP	10-308283	11/1998
JP	03-019211	1/1991	JP	11-269652	10/1999
JP	03-022569	1/1991	JP	2000-031387	1/2000
JP	03-023294	1/1991	JP.	2000-058777	2/2000
JP JP	03-023299 03-044967	1/1991 2/1991	JP JP	2000-068072 2000-087029	3/2000 3/2000
JΡ	03-048421	3/1991	ne Ne	2000-319772	3/2000
JP	03-070124	3/1991	ÎP.	2000-138094	5/2000
JP	03-185716	8/1991	JP	2000-218445	8/2000
JP	03-208885	9/1991	IP.	2000-319772	11/2000
JP	03-234025	10/1991	<u>r</u>	2000-340883	12/2000
JP JP	03-286522 03-286531	12/1991 12/1991	JP JP	2000-353666	12/2000 12/2000
JP	04-031391	2/1992	JP JP	2001-111000 2001-020075	1/2001
JP	04-031396	2/1992	JP ,r	2001-62244	3/2001
JP	04-031396 A	2/1992	JP	2001-152339	6/2001
JP	04-100292	4/1992	JP	2001-172767	6/2001
JP	04-111418	4/1992	JP	2001-189312	7/2001
JP	04-132214	5/1992	JP	2001-217206	8/2001
1P	04-132681	5/1992	JP	2001-220287	8/2001

JP	2001-220294	8/2001
JP	2001-240972	9/2001
JP	2001-254181	9/2001
1b	2001-284042	10/2001
JP	2001-303251	10/2001
JP	2001-328900	11/2001
WO	90/02216	3/1990
wo	WO/91/00510	1/1991
wo	93/02111 A1	2/1993
WO	96/17107 A1	6/1996
wo	96/18756 A1	6/1996
wo	98/06889	2/1998
WO	98/51838	11/1998
wo	WO 98/51838	11/1998
wo	WO/99/01595	1/1999
WO	99/01595	1/1999
wo	99/13504	3/1999
wo "	99/29924	6/1999
wo	WO/99/29924	6/1999
WO	99/41423 A2	8/1999
wo	WO 99/65064	12/1999
wo	00/11721	3/2000
WO	00/15865	3/2000
WO	WO/00/15865	3/2000
wo	00/15881 A2	3/2000
wo	00/16377 A2	3/2000
WO	00/54320 A1	9/2000
wo	WO 00/54320	9/2000
wo	00/63957 A1	10/2000
wo	00/79019 Ai	12/2000
wo	00/79576 A1	12/2000
wo	00/79576	12/2000
wo	01/15220 A1	3/2001
WO	01/15220	3/2001
WO	WO 01/17692	3/2001
WO	01/27346 A1	4/2001
WO WO	01/27347 A1	4/2001
	01/29280 A1	4/2001
WO	01/29891 A1	4/2001
WO WO	01/29893 A1	4/2001
WO WO	01/36702 A1	5/2001
	01/40541 A1	6/2001
WO WO	01/66832 A2	9/2001
₩O	WO 02/01628 A2	1/2002
wo Wo	WO 02/08488	1/2002
WO WO	02/45167	6/2002
WO WO	WO 02/45871 A1	6/2002
WU	02/067319	8/2002

### OTHER PUBLICATIONS

Ritala, et al. "Atomic Force Microscopy Study of Titanium Dioxide Thin Films Grown by Atomic Layer Epitaxy," Thin Solid Films, vol. 228, No. 1-2 (May 15, 1993), pp. 32-35. Ritala, et al. "Growth of Titanium Dioxide Thin Films by

Atomic Layer Epitaxy," Thin Solid Films, vol. 225 No. 1-2 (Mar. 25, 1993) pp. 288-295.

Min, et al. "Chemical Vapor Deposition of Ti-Si-N Films With Alternating Source Supply," Mat. Rec. Soc. Symp. Proc. vol. (1999).

Klaus, et al. "Atomically Controlled Growth of Tungsten and Tungsten Nitride Using Sequential Surface Reactions," Applied Surface Science, 162–163 (2000) 479–491.

PCT International Search Report from International Application No. PCT/US02/19481, Dated Jan. 8, 2003.

Kitagawa et al. Hydrogen-mediated low-temperature epitaxy of Si in plasma-enhanced chemical vapor deposition. Applied Surface Science. pp. 30-34 (2000). Kians et al. Atomically controlled growth of tungsten and tungsten nitride using sequential surface reacions. Applied Surface Science, pp. 479-491(2000).

Hultman, et al., "Review of the thermal and mechanical stability of TiN-based thin films", Zeitschrift Fur Metallkunde, 90(10) (Oct. 1999), pp. 803-813.

Klaus, et al., "Atomic Layer Deposition of SiO2 Using Catalyzed and Uncatalyzed Self-Limiting Surface Reactions", Surface Reviews & Letters, 6(3&4) (1999), pp. 435-448.

Yamaguchi, et al., "Atomic-layer chemical-vapor-deposition of silicon dioxide films with extremely low hydrogen content", Appl. Surf. Sci., vol. 130-132 (1998), pp. 202-207.

George, et al., "Surface Chemistry for Atomic Layer Growth", J. Phys. Chem., vol. 100 (1996), pp. 13121-13131.

George, et al., "Atomic layer controlled deposition of SiO2 and Al2O3 using ABAB... binary reaction sequence chemistry", Appl. Surf. Sci., vol. 82/83 (1994), pp. 460-467. Wise, et al., "Diethyldiethoxysilane as a new precursor for SiO2 growth on silicon", Mat. Res. Soc. Symp. Proc., vol. 334 (1994), pp. 37-43.

Niinisto, et al., "Synthesis of oxide thin films and overlayers by atomic layer epitaxy for advanced applications", Mat. Sci. & Eng., vol. B41 (1996), pp. 23-29.

Ritala, et al., "Perfectly conformal TiN and Al2O3 films deposited by atomic layer deposition", Chemical Vapor Deposition, vol. 5(1) (Jan. 1999), pp. 7-9.

Min, et al., "Atomic layer deposition of TiN thin films by sequential introduction of Ti precursor and Nh/sub3/". Symp.: Advanced Interconnects and Contact Materials and Processes for Future Integrated Circuits (Apr. 13–16, 1998), pp. 337–342.

Klans, et al., "Atomic Layer Deposition of Tungsten using Sequential Surface Chemistry with a Sacrificial Stripping Reaction," Thin Solid Films 360 (2000), pp. 145-153, (Accepted Nov. 16, 1999).

Min, et al., "Metal-Organic Atomic-Layer Deposition of Titanium-Silicon-Nitride Films", Applied Physics Letters, American Inst. Of Physics, vol. 75(11) (Sept. 13, 1999).

Martensson, et al., "Atomic Layer Epitaxy of Copper on Tantahum", Chemical Vapor Deposition, 3(1) (Feb. 1, 1997), pp. 45-50.

Ritala, et al. "Atomic Layer Epitaxy Growth of TiN Thin Films", J. Electrochem. Soc., 142(8) (Aug. 1995), pp. 2731-2737.

Elers, et al., "NbC15 as a precursor in atomic layer epitaxy", Appl. Surf. Sci., vol. 82/83 (1994), pp. 468-474.

Lee, "The Preparation of Titanium-Based Thin Film by CVD Using Titanium Chlorides as Precursors", Chemical Vapor Deposition, 5(2) (Mar. 1999), pp. 69-73.

Martensson, et al., "Atomic Layer Epitaxy of Copper, Growth & Selectivity in the Cu (II)-2,2.6,6-Tetramethyl-3, 5-Heptanedion ATE/H2 Process", J. Electrochem. Soc., 145(8) (Aug. 1998), pp. 2926-2931.

Min, et al., "Chemical Vapor Deposition of Ti-Si-N Films with Alternating Source Supply", Mat., Res. Soc. Symp. Proc., vol. 564 (Apr. 5, 1999), pp. 207-210.

Bedair, "Atomic layer epitaxy deposition processes", J. Vac. Sci. Techol. 12(1) (Jan./Feb. 1994).

Yamaga, et al., "Atomic layer epitaxy of ZnS by a new gas supplying system in a low-pressure metalorganic vapor phase epitaxy", J. of Crystal Growth 117 (1992), pp. 152-155.

Elam, et al., "Nucleation and growth during tungsten atomic layer deposition on SiO2 surfaces," Thin Solid Films 386 (2001) np. 41...52 (Accepted Dec. 14, 2000)

(2001) pp. 41-52, (Accepted Dec. 14, 2000). Ohba, et al., "Thermal Decomposition of Methylhydrazine and Deposition Properties of CVD TiN Thin Films", Conference Proceedings, Advanced Metallization for ULSI Applications in 1993 (1994), pp. 143-149.

Scheper, et al., "Low-temperature deposition of titanium nitride films from dialkylhydrazine-based precursors", Materials Science in Semiconductor Processing 2 (1999), pp. 149-157.

Suzuki, et al., "A 0.2-µm contact filing by 450° C-hydrazine-reduced TiN film with low resistivity", IEDM 92-979, pp. 11.8.1-11.8.3.

Suzuki, et al., 'LPCVD-TiN Using Hydrazine and TiCl4", VMIC Conference (Jun. 8-9, 1993), pp. 418-423.

IBM Tech. Disc. Bull. Knowledge-Based Dynamic Scheduler in Distributed Computer Control, (Jun. 1990), pp. 80-84.

IBM Tech. Disc. Bull. "Multiprocessor and Multitasking Architecture for Tool Control of the Advanced via Inspection Tools" (May 1992), pp. 190-191.

McGeachin, S., "Synthesis and properties of some  $\beta$ -diketimines derived from acetylacetone, and their metal complexes", Canadian J. of Chemistry, vol. 46 (1968), pp. 1903-1912.

Solanki, et al., "Atomic Layer deposition of Copper Seed Layers", Electrochemical and Solid State Letters, 3(10) (2000), pp. 479-480.

NERAC.COM Retro Search: Atomic Layer Deposition of Copper, dated Oct. 11, 2001.

NERAC.COM Retro Search: Atomic Layer Deposition/ Epitaxy Aluminum Oxide Plasma, dated Oct. 2, 2001. NERAC Search abstract of "Atomic Layer deposition of Ta and Ti for Interconnect Diffusion Barriers", by Rossnagel, et al., J. Vac. Sci. & Tech., 18(4) (Jul. 2000).

Abstracts of articles re atomic layer deposition.

Abstracts of search results re atomic layer deposition, search dated Jan. 24, 2002.

Abstracts of articles re atomic layer deposition and atomic layer nucleation.

Abstracts of articles re atomic layer deposition and semiconductors and copper.

Abstracts of articles—atomic layer deposition.

NERAC Search—Atomic Layer Deposition, search dated Oct. 16, 2001.

Bader, et al., "Integrated Processing Equipment", Solid State Technology, Cowan Pub., vol. 33, No. 5 (May 1, 1990), pp. 149-154.

Choi, et al., "The effect of annealing on resistivity of low pressure chemical vapor depositied titanium diboride", J. Appl. Phys. 69(11) (Jun. 1, 1991), pp. 7853-7861.

Choi, et al., "Stability of TiB2 as a Diffusion Barrier on Silicon", J. Electrochem. Soc. 138(10) (Oct. 1991), pp. 3062-3067.

"Cluster Tools for Fabrication of Advanced devices" Jap. I. of Applied Physics, Extended Abstracts, 22nd Conference Solid State Devices and Materials (1990), pp. 849-852 XP000178141.

"Applications of Integrated processing", Solid State Technology, US, Cowan Pub., vol. 37, No. 12 (Dec. 1, 1994), pp. 45-47.

Kitigawa, et al., "Hydrogen-mediated low temperature epitaxy of Si in plasma-enhanced chemical vapor deposition", Applied Surface Science (2000), pp. 30-34.

Lee, et al., "Pulsed nucleation for ultra-high aspect ratio tungsten plugfill", Novellus Systems, Inc. (2001), pp. 1-2.

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6,849,545 B2

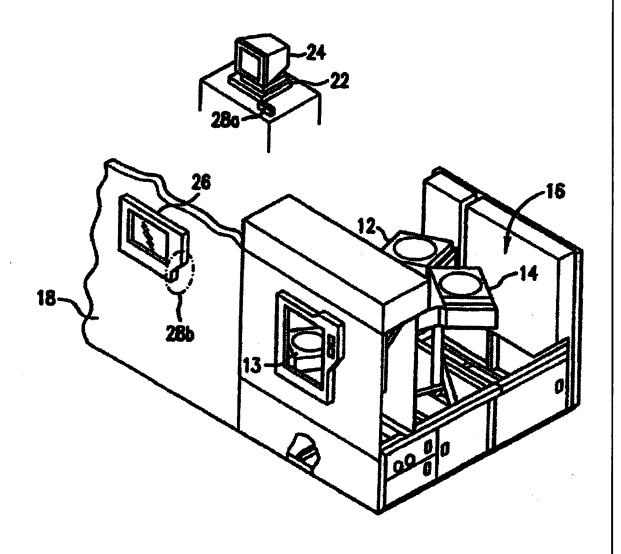
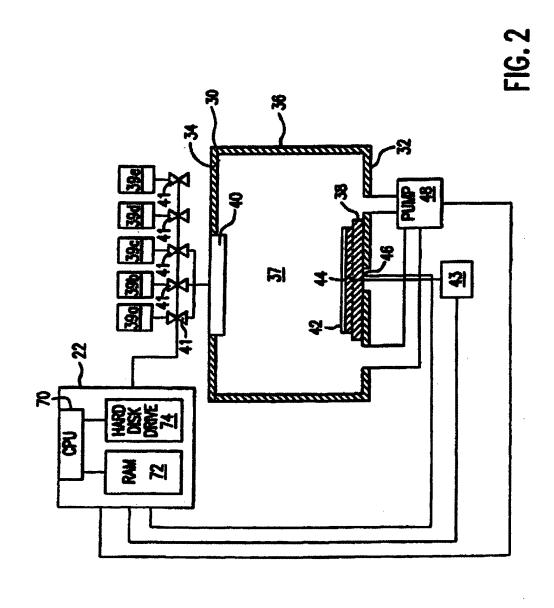


FIG. 1

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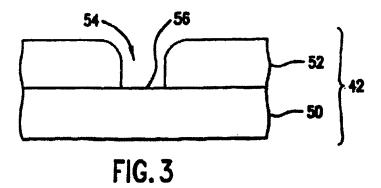


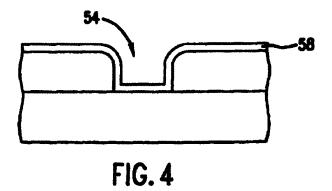
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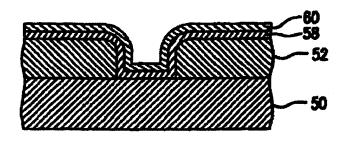
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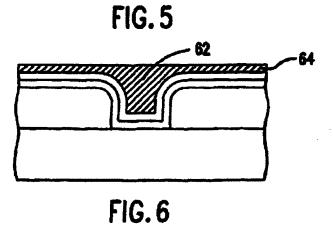
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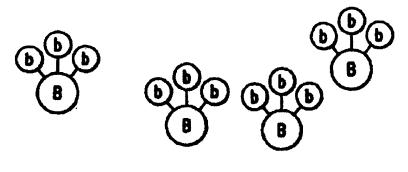




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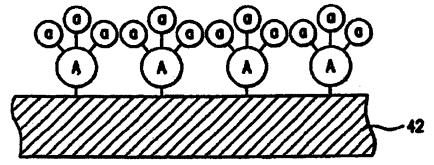


FIG. 7

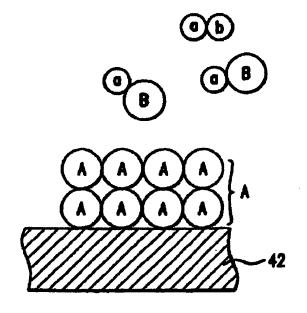
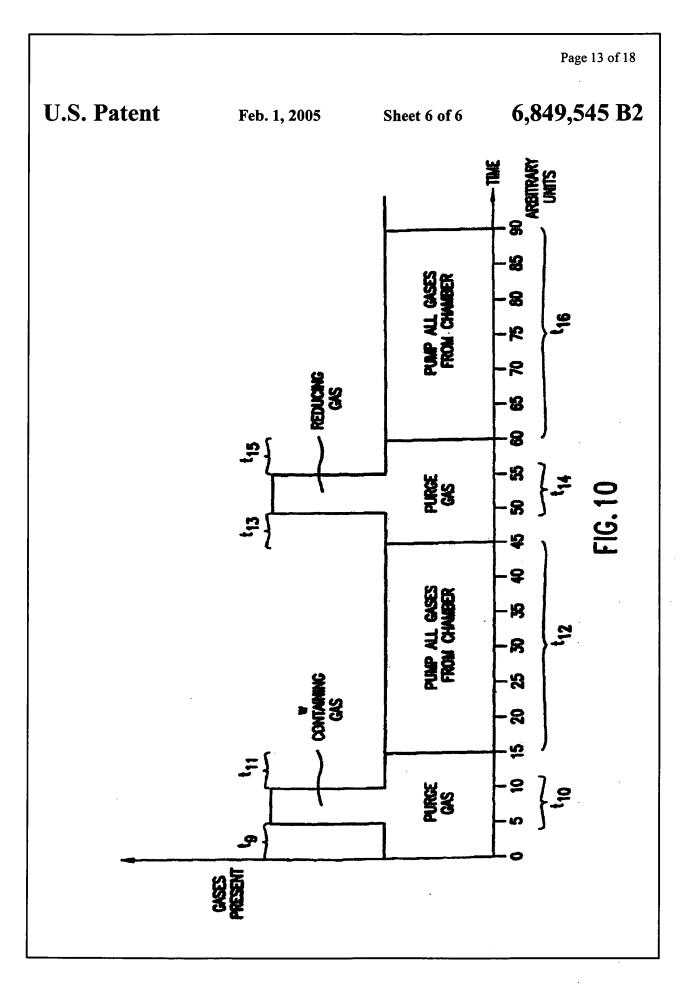


FIG. 8



# SYSTEM AND METHOD TO FORM A COMPOSITE FILM STACK UTILIZING SEQUENTIAL DEPOSITION TECHNIQUES

#### BACKGROUND OF THE INVENTION

This invention relates to the processing of semiconductor substrates. More particularly, this invention relates to improvements in the process of forming contacts.

Formation of contacts in multi-level integrated circuits poses many challenges to the semiconductor industry as the drive to increase circuit density continues, due to the reduction in size of the circuit features. Contacts are formed by depositing conductive interconnect material in an opening on the surface of insulating material disposed between two spaced-apart conductive layers. The aspect ratio of such an opening inhibits deposition of conductive interconnect material that demonstrates satisfactory step coverage and gap-fill, employing traditional interconnect material such as aluminum. In addition, diffusion between the aluminum and the surrounding insulating material often occurs, which adversely effects operation of the resulting electrical circuits.

Barrier materials have been introduced to improve both 25 the step coverage and gap-fill of aluminum, while limiting diffusion of the same. Barrier materials must also provide good adhesion properties for aluminum. Otherwise, the thermal and electrical conductance of the resulting contact may be compromised. Examples of barrier materials providing the aforementioned characteristics include TiN, TiW, TiB<sub>2</sub>, TiC and Ti<sub>2</sub>N.

However, attempts have been made to provide interconnect material with lower electrical resistivity than aluminum. This has led to the substitution of copper aluminum. Sopper, like aluminum, also suffers from diffusion characteristics and may form undesirable intermetallic alloys that reduce the availability of suitable barrier materials.

Tungsten has proved to be a suitable barrier material that effectively prevents diffusion of copper. Typically deposited employing chemical vapor deposition (CVD) techniques, tungsten deposition is attendant with several disadvantages. Tungsten diffuses easily into surrounding dielectric material. In addition, tungsten has proven difficult to deposit uniformly. This has been shown by variance in tungsten layers' thickness of greater than 1%. As result, it is difficult to control the resistivity of a tungsten layer.

What is needed, therefore, are improved techniques to form barrier layers for copper interconnects that include tungsten.

#### SUMMARY OF THE INVENTION

One embodiment of the present invention is directed to a method to form a stacked barrier layer on a substrate disposed in a processing chamber by serially exposing the substrate to first and second reactive gases to form an adhesion layer. The adhesion layer is then serially exposed to third and fourth reactive gases to form a barrier layer adjacent to the adhesion layer. A copper layer is disposed adjacent to the barrier layer. To that end, another embodiment of the invention is directed to a system to carry out the method.

### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a perspective view of a semiconductor processing system in accordance with the present invention;

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FIG. 2 is a detailed view of the processing chambers shown above in FIG. 1;

FIG. 3 is a detailed cross-sectional view of a substrate shown above in FIG. 2 before deposition of a first refractory metal layer in accordance with one embodiment of the present invention;

FIG. 4 is a detailed cross-sectional view of the substrate shown above in FIG. 3 after deposition of a first refractory metal layer in accordance with one embodiment of the present invention;

FIG. 5 is a detailed cross-sectional view of a substrate shown above in FIG. 4 after deposition of a second refractory metal layer in accordance with one embodiment of the present invention;

FIG. 6 is a detailed cross-sectional view of a substrate shown above in FIG. 2 after deposition of a copper contact in accordance with one embodiment of the present invention:

PIG. 7 is a schematic view showing deposition of a first molecule onto a substrate during sequential deposition techniques in accordance with one embodiment of the present invention:

FIG. 8 is a schematic view showing deposition of second molecule onto a substrate during sequential deposition techniques in accordance with one embodiment of the present invention:

FIG. 9 is a graphical representation showing the concentration of gases introduced into the processing chamber shown above in FIG. 2, and the time in which the gases are present in the processing chamber to deposit the Titanium refractory metal layer shown above in FIG. 4, in accordance with one embodiment of the present invention; and

FIG. 10 is a graphical representation showing the concentration of gases introduced into the processing chamber shown above in FIG. 2, and the time in which the gases are present in the processing chamber to deposit the Tungsten layer shown above in FIG. 4, in accordance with one embodiment of the present invention.

## DETAILED DESCRIPTION OF THE INVENTION

Referring to FIG. 1, an exemplary wafer processing 45 system includes one or more processing chambers 12, 13 and 14 disposed in a common work area 16 surrounded by a wall 18. Processing chambers 12 and 14 are in data communication with a controller 22 that is connected to one or more monitors, shown as 24 and 26. Monitors 24 and 26 typically display common information concerning the process associated with the processing chambers 12 and 14. Monitor 26 is mounted to the wall 18, with monitor 24 being disposed in the work area 16. Operational control of processing chambers 12 and 14 may be achieved with use of a light pen, associated with one of monitors 24 and 26, to communicate with controller 22. For example, a light pen 28a is associated with monitor 24 and facilitates communication with the controller 22 through monitor 24. A light pen 28b facilitates communication with controller 22 through

Referring both the to FIGS. 1 and 2, each of processing chambers 12 and 14 includes a housing 30 having a base wall 32, a cover 34, disposed opposite to the base wall 32, and a sidewall 36, extending thereberween. Housing 30 defines a chamber 37, and a pedestal 38 is disposed within processing chamber 37 to support a substrate 42, such as a semiconductor wafer. Pedestal 38 may be mounted to move

between the cover 34 and base wall 32, using a displacement mechanism (not shown), but is typically fixed proximate to bottom wall 32. Supplies of processing gases 39a, 39b, 39c, 39d and 39e are in fluid communication with the processing chamber 37 via a showerhead 40. Regulation of the flow of gases from supplies 39a, 39b and 39c is effectuated via flow values 41

Depending on the specific process, substrate 42 may be heated to a desired temperature prior to layer deposition via a heater embedded within pedestal 38. For example, pedestal 38 may be resistively heated by applying an electric current from an AC power supply 43 to a heater element 44. Substrate 42 is, in turn, heated by pedestal 38, and can be maintained within a desired process temperature range of, for example, about 20° C. to about 750° C., with the actual temperature varying dependent upon the gases employed and the topography of the surface upon which deposition is to occur. A temperature sensor 46, such as a thermocouple, is also embedded in the wafer support pedestal 38 to monitor the temperature of the pedestal 38 in a conventional manner. 20 For example, the measured temperature may be used in a feedback loop to control the electrical current applied to heater element 44 by the power supply 43, such that the wafer temperature can be maintained or controlled at a desired temperature the is suitable for the particular process 25 application. Pedestal 38 is optionally heated using radiant heat (not shown). A vacuum pump 48 is used to evacuate processing chamber 37 and to help maintain the proper gas flows and pressure inside processing chamber 37.

Referring to FIGS. 1 and 3, one or both of processing chambers 12 and 14, discussed above may operate to form, on substrate 42, a contact in accordance with the present invention on substrate 42. To that end, substrate 42 includes a wafer 50 that may be formed from any material suitable for semiconductor processing, such as silicon. One or more layers, shown as layer 52, may be present on wafer 50. Layer 52 may be formed from any suitable material, including dielectric or conductive materials. Layer 52 includes a void 54, exposing a region 56 of substrate 42.

Referring to FIG. 4, formed adjacent to layer 52 and region 54 is a layer containing a refractory metal compound, such as titanium. In the present example, layer 58 is formed from titanium nitride, TiN, by sequentially exposing substrate 42 to processing gases to chemisorb monolayers of differing compounds onto the substrate, discussed more fully below. Layer 58 conforms to the profile of the void 54 so as to cover region 56 and layer 52.

Referring to FIG. 5, adjacent to layer 58 is formed an additional refractory metal layer 60. In the present example, so layer 60 is formed from tungsten in the manner discussed above with respect to layer 52, except using different process gases. Layer 60 conforms to the profile of layer 58 and, therefore, conforms to the profile of void 54.

Referring to FIG. 6, shown is one example of a contact 62 st formed in void 54 in accordance with the present invention by deposition of a layer of copper 64 that fills void 54, using standard deposition techniques. With this configuration, a stacked barrier layer consisting of TiN layer 58 and W layer 60 surrounds contact 62. TiN layer 58 serves as an adhesion 60 layer to facilitate nucleation and deposition by W layer 60. TiN layer also serves as a diffusion barrier to reduce, if not prevent, diffusion of W into the surrounding environs, such as region 56 and layer 52. W layer 60 serves as a barrier layer for contact 62, thereby preventing copper material 65 from diffusing into or through TiN layer 58 and into the environs surrounding void 54. Employing sequential depo-

sition techniques, such as atomic layer deposition, provides superior thermal and conductive characteristics of the aforementioned stacked barrier layer. Specifically, the sequential deposition techniques described below enable precise control over the thickness of both layers 58 and 60.

Referring to FIGS. 1, 6 and 7, one or both of processing chambers 12 and 14, discussed above, may operate to deposit layers 58 and 60 on substrate 42 employing sequential deposition techniques. Specifically, the initial surface of substrate 42, e.g., the surface of region 56 and the surface of layer 52, presents an active ligand to the process region. A batch of a first processing gas, in this case Aa, results in a layer of A being deposited on substrate 42 having a surface of ligand x exposed to the processing chamber 37. Thereafter, a purge gas enters processing chamber 37 to purge the gas Aa\_ After purging gas Aa\_ from processing chamber 37, a second batch of processing gas, Bb,, is introduced into processing chamber 37. The a ligand present on the substrate surface reacts with the b ligand and B atom, releasing molecules ab and Ba, that move away from substrate 42 and are subsequently pumped from processing chamber 37. In this manner, a surface comprising a monolayer of A atoms remains upon substrate 42 and exposed to processing chamber 37, shown in FIG. 4. The process proceeds cycle after cycle, until the desired thickness is achieved.

Referring to both FIGS. 2 and 8, although any type of processing gas may be employed, in the present example, the processing gas Aa, is a titanium-containing gas selected from the group that includes TDMAT, TDEAT and TiCl4. The processing gas Bb, functions as a reducing agent and is selected from the group including  $H_2$ ,  $B_2H_6$ ,  $SiH_4$  and  $NH_3$ . Two purge gases were employed: Ar and N2. Each of the processing gases is flowed into processing chamber 37 with a carrier gas, which in this example, is one of the purge gases. It should be understood, however, that the purge gas may differ from the carrier gas, discussed more fully below. One cycle of the sequential deposition technique in accordance with the present invention includes flowing a purge 40 gas into processing chamber 37 during time t<sub>1</sub> before the titanium-containing gas is flowed into processing chamber 37. During time t, the titanium-containing processing gas is flowed into the processing chamber 37, along with a carrier gas. After t2 has lapsed, the flow of titanium-containing gas terminates and the flow of the carrier gas continues during time t3, purging the processing chamber of the titaniumcontaining processing gas. During time t4, the processing chamber 37 is pumped so as to remove all gases. After pumping of process chamber 37, a carrier gas is introduced during time t<sub>5</sub>, after which time the reducing process gas is introduced into the processing chamber 37 along with the carrier gas, during time to. The flow of the reducing process gas into processing chamber 37 is subsequently terminated. After the flow of reducing process gas into processing chamber 37 terminates, the flow of carrier gas continues, during time t<sub>7</sub>. Thereafter, processing chamber 37 is pumped so as to remove all gases therein, during time te, thereby concluding one cycle of the sequential deposition technique in accordance with the present invention. The aforementioned cycle is repeated multiple times until layer 58 reaches a desired thickness. After TiN layer 58 reaches a desired thickness, W layer 60 is deposited adjacent thereto employing sequential deposition techniques.

Referring to FIGS. 2 and 10 to form W layer 60, processing gas Aa, may be any known tungsten-containing gas, such a tungsten hexafluoride, WF<sub>6</sub>. The processing gas Bb, functions as a reducing agent and is selected from the group

including SiH4, B2H6 and NH3. The same purge gases may be employed, as discussed above. Each of the processing gases is flowed into the processing chamber 37 with a carrier gas, as discussed above. One cycle of the sequential deposition technique to form W layer 60 in accordance with the present invention includes flowing a purge gas into the processing chamber 37 during time to before the tungstencontaining gas is flowed into the processing chamber 37. During time tio, the tungsten-containing processing gas is flowed into the processing chamber 37, along with a carrier gas. After time t10 has lapsed, the flow of tungstencontaining gas terminates and the flow of the carrier gas continues during time  $t_{11}$ , purging the processing chamber of the tungsten-containing processing gas. During time tize processing chamber 37 is pumped so as to remove all gases. After pumping of the process chamber 37, a carrier gas is introduced during time t<sub>1,3</sub>, after which time the reducing process gas is introduced into the processing chamber 37 along with the carrier gas, during time t14. The flow of the reducing process gas into processing chamber 37 is subse- 20 quently terminated. After the flow of reducing process gas into the processing chamber 37 terminates, the flow of carrier continues during time t15. Thereafter, the processing chamber 37 is pumped so as to remove all gases therein, during time t<sub>16</sub>, thereby concluding one cycle of the sequen- 25 tial deposition technique in accordance with the present invention. The aforementioned cycle is repeated multiple times until layer 60 reaches a desired thickness. After W layer 60 reaches a desired thickness, the contact 62, shown in FIG. 6 may be deposited employing known techniques. 30

The benefits of employing sequential deposition are manifold, including flux-independence of layer formation that provides uniformity of deposition independent of the size of a substrate. For example, the measured difference of the layer uniformity and thickness measured between of 200 35 mm substrate and a 300 mm substrate deposited in the same chamber is negligible. This is due to the self-limiting characteristics of chemisorption. Purther, the chemisorption characteristics contribute to near-perfect step coverage over complex topography.

In addition, the thickness of the layers 58 and 60 may be easily controlled while minimizing the resistance of the same by employing sequential deposition techniques. In one example of the present invention, layers 58 and 60, as well as contact 62 may be deposited in a common processing 45 chamber, for example chambers 12 and 14. To provide added flexibility when depositing layers 58 and 60, as well as contact 62, a bifurcated deposition process may be practiced in which layer 58 is deposited in one process chamber, for example chamber 12, and layer 60 is deposited in a separate 50 chamber, for example chamber 14. This may reduce the deposition time of each of layers 58 and 60 by, inter alia, having each processing chamber 12 and 14 preset to carryout the process parameters necessary to deposit the requisite refractory metal layers.

Referring again to FIG. 2, the process for depositing the tungsten layer may be controlled using a computer program product that is executed by the controller 22. To that end, the controller 22 includes a central processing unit (CPU) 70, a volatile memory, such as a random access memory (RAM) 60 72 and permanent storage media, such as a floppy disk drive for use with a floppy diskette, or hard disk drive 74. The computer program code can be written in any conventional computer readable programming language; for example, 68000 assembly language, C, C++, Pascal, Fortran, and the 65 like. Suitable program code is entered into a single file, or multiple files, using a conventional text editor and stored or

embodied in a computer-readable medium, such as the hard disk drive 74. If the entered code text is in a high level language, the code is compiled and the resultant compiler code is then linked with an object code of precompiled Windows® library routines. To execute the linked and compiled object code the system user invokes the object code, causing the CPU 70 to load the code in RAM 72. The CPU 70 then reads and executes the code to perform the tasks identified in the program.

Although the invention has been described in terms of specific embodiments, one skilled in the art will recognize that various changes to the reaction conditions, i.e., temperature, pressure, film thickness and the like can be substituted. Further, the sequence of gases may utilize a different initial sequence. For example, the initial sequence may include exposing the substrate to the reducing gas before the metal-containing gas is introduced into the processing chamber. In addition, other stacked layers may be deposited, in addition to the refractory-metal layers described above and for purposes other than formation of a barrier layer. Therefore, the scope of the invention should not be based upon the foregoing description. Rather, the scope of the invention should be determined based upon the claims recited herein, including the full scope of equivalents thereof.

What is claimed is:

1. A method for forming a stacked barrier layer on a substrate disposed in a processing chamber, comprising: serially exposing said substrate to first and second reactive gases to form an adhesion layer, and

serially exposing said adhesion layer to third and fourth reactive gases to form a barrier layer adjacent to said adhesion layer.

2. The method as recited in claim 1 further including depositing a layer of copper adjacent to said barrier layer.

3. The method as recited in claim 1 further including repeating serially exposing said substrate to first and second reactive gases to form said adhesion layer to a desired thickness before serially exposing said adhesion layer to third and fourth reactive gases.

4. The method as recited in claim 3 further including repeating serially exposing said substrate to third and fourth reactive gases to form said barrier layer to a desired thickness after serially exposing said substrate to first and second reactive gases.

5. The method as recited in claim 1 further including providing first and second processing chambers wherein serially exposing said substrate to first and second reactive gases further includes serially exposing said substrate to said first and second reactive gases while said substrate is disposed in said first processing chamber and serially exposing said adhesion layer to third and fourth reactive gases further includes serially exposing said adhesion layer to third and fourth reactive gases while said substrate is positioned in said second processing chamber.

6. The method as recited in claim 3 further including providing first and second processing chambers wherein serially exposing said substrate to first and second reactive gases further includes serially exposing said substrate to said first and second reactive gases while said substrate is disposed in said first processing chamber and scrially exposing said adhesion layer to third and fourth reactive gases further includes serially exposing said adhesion layer to third and fourth reactive gases while said substrate is positioned in said first processing chamber and depositing a layer of copper adjacent to said barrier layer further includes depositing a copper layer adjacent to said barrier layer when said substrate is positioned in said second processing chamber.

7. The method as recited in claim 1 further including providing first, second and third processing chambers wherein serially exposing said substrate to first and second reactive gases further includes serially exposing said substrate to said first and second reactive gases while said substrate is disposed in said first processing chamber and serially exposing said adhesion layer to third and fourth reactive gases further includes serially exposing said adhesion layer to third and fourth reactive gases while said substrate is positioned in said second processing chamber and depositing a layer of copper adjacent to said barrier layer further includes depositing a copper layer adjacent to said barrier layer when said substrate is positioned in said third processing chamber.

8. The method as recited in claim 1 wherein serially exposing said substrate further includes introducing said second reactive gas into said processing chamber and further including purging said processing chamber of said second reactive gas before exposing said adhesion layer to said third

reactive gas.

9. The method as recited in claim 1 wherein said first and 20 third gases each includes a refractory metal compound, with the refractory metal compound associated with said first reactive gas differing from the refractory metal compound associated with said third reactive gas.

10. The method as recited in claim 1 wherein said first 25 reactive gas is selected from the group consisting of TDMAT, TDEAT and TiCl4 and said second reactive gas is selected from the group consisting of H2, B2H6, SiH4 and

NH<sub>2</sub>

11. The method as recited in claim 1 wherein said third reactive gas is WP6 and said fourth reactive gas is selected from the group consisting of SiH4, B2H6 and NH3

12. The method as recited in claim 1 further comprising purging said processing chamber of said first reactive gas before introducing said second reactive gas by introducing a 35 purge gas into said processing chamber after exposing said substrate to said first reactive gas and before exposing said substrate to said second reactive gas.

13. The method as recited in claim 1 further comprising purging said processing chamber of said first reactive gas before introducing said second reactive gas by pumping said processing chamber clear of said first reactive gas before

introducing said second reactive gas.

14. The method as recited in claim 1 further comprising purging said processing chamber of said third reactive gas 45 before introducing said fourth reactive gas by introducing a purge gas into said processing chamber after exposing said substrate to said third reactive gas and before exposing said substrate to said fourth reactive gas.

15. The method as recited in claim 1 further comprising 50 TiCl4, or combinations thereof. purging said processing chamber of said third reactive gas before introducing said fourth reactive gas by pumping said processing chamber clear of said third reactive gas before introducing said fourth reactive gas.

16. A method for forming a stacked barrier layer on a 55 thereof. substrate disposed in a processing chamber, said method

serially exposing said substrate to first and second reactive gases to form an adhesion layer by introducing said first reactive gas into said processing chamber and removing said first reactive gas from said processing chamber before introducing said second reactive gas; repeating serially exposing said substrate to first and second reactive gases to form said adhesion layer to a

desired thickness;

serially exposing said adhesion layer to third and fourth reactive gases to form a barrier layer adjacent to said

adhesion layer by introducing said third reactive gas into said processing chamber and clearing said third reactive gas from said processing chamber before introducing said fourth reactive gas;

repeating serially exposing said substrate to third and fourth reactive gases to form said barrier layer to an

acceptable thickness;

purging said processing chamber of said first and second reactive gases before introducing either of said third

and fourth reactive gases; and

depositing a layer of copper adjacent to said barrier layer. 17. The method as recited in claim 16 wherein said first reactive gas is selected from the group consisting of TDMAT, TDEAT and TiCl4, said second reactive gas is selected from the group consisting of H2, B2H6, SiH4 and  $NH_3$ , said third reactive gas is  $WF_6$ , and said fourth reactive gas is selected from the group consisting of  $SiH_4$ ,  $B_2H_6$  and

18. The method as recited in claim 16 further comprising removing said first reactive gas from said processing chamber before introducing said second reactive gas by introducing an inert gas into said processing chamber, and clearing said third reactive gas from said processing chamber before introducing said fourth reactive gas by introducing an expul-

sion gas into said processing chamber.

19. The method as recited in claim 16 further comprising removing said first reactive gas from said processing chamber before introducing said second reactive gas by pumping said processing chamber clear of said first reactive gas, and clearing said third reactive gas from said processing chamber by pumping said processing chamber clear of said third

20. A method for forming a stacked barrier layer on a substrate surface, comprising:

exposing the substrate surface to a first reactive gas;

exposing the substrate surface to a second reactive gas; sequentially repeating the exposure to the first and second reactive gases until an adhesion layer having a desired

exposing the substrate surface to a third reactive gas; exposing the substrate surface to a fourth reactive gas; and then

sequentially repeating the exposure to the third and fourth reactive gases until a barrier layer having a desired thickness is formed over the adhesion layer.

21. The method of claim 20, wherein the first reactive gas comprises a refractory metal-containing compound.

22. The method of claim 21, wherein the refractory metal-containing compound comprises TDMAT, TDEAT,

23. The method of claim 21, wherein the second precursor gas comprises a reducing compound.

24. The method of claim 23, wherein the reducing compound comprises H<sub>2</sub>, B<sub>2</sub>H<sub>6</sub>, SiH<sub>4</sub>, NH<sub>3</sub>, or combinations

25. The method of claim 21, wherein the third precursor gas comprises a refractory metal-containing compound.

26. The method of claim 25, wherein the refractory metal-containing compound comprises tungsten.

27. The method of claim 21, wherein the fourth comprises a reducing compound.

28. The method of claim 27, wherein the reducing compound comprises SiH<sub>4</sub>, B<sub>2</sub>H<sub>6</sub>, NH<sub>3</sub>, or combinations thereof.

29. The method of claim 20, further comprising deposit-65 ing copper at least partially over the barrier layer.

30. The method of claim 20, wherein the adhesion layer is deposited within a first processing chamber.

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31. The method of claim 30, wherein the barrier layer is deposited within a second processing chamber.

32. The method of claim 31, wherein the copper is

deposited in a third processing chamber.

- 33. The method of claim 32, wherein the first, second and 5 third processing chambers are each disposed about a common mainframe.
- 34. The method of claim 30, wherein the adhesion layer and the barrier layer are both deposited in the first chamber.
- 35. A method for depositing a barrier layer on a substrate 10 surface, comprising:
  - sequentially exposing the substrate surface to a first refractory metal-containing compound and a first reducing compound; and
  - sequentially exposing the substrate surface to a second refractory metal-containing compound and a second reducing compound to form the barrier layer.
- 36. The method of claim 35, wherein the first refractory metal-containing compound comprises TDMAT, TDEAT, TiCl<sub>a</sub>, or combinations thereof.

37. The method of claim 35, wherein the second refractory metal-containing compound comprises tungsten.

- 38. The method of claim 35, wherein the first and second reducing compounds is selected from a group consisting of SiH<sub>4</sub>, B<sub>2</sub>H<sub>6</sub>, NH<sub>3</sub>, and combinations thereof.
- 39. The method of claim 35, wherein the barrier layer comprises titanium, titanium nitride, tungsten, tungsten nitride, or combinations thereof.
- 40. The method of claim 35, wherein the adhesion layer is deposited within a first processing chamber and the barrier layer is deposited within a second processing chamber.
- 41. The method of claim 35, further comprising depositing copper at least partially over the barrier layer.

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42. The method of claim 41, wherein the adhesion layer is deposited within a first processing chamber and the barrier layer is deposited within a second processing chamber.

43. The method of claim 42, wherein the copper is deposited in a third processing chamber and the first, second and third processing chambers are each disposed about a common mainframe.

44. The method of claim 42, wherein the adhesion layer and the barrier layer are both deposited in the first chamber.

45. A method for forming a metal contact on a substrate

surface, comprising:

- sequentially exposing the substrate surface to a titaniumcontaining compound and a nitrogen-containing compound to form an adhesion layer comprising titanium nitride;
- sequentially exposing the substrate surface to a tungstencontaining compound and a reducing compound to form a barrier layer comprising tungsten; and
- depositing copper at least partially over the barrier layer to form the metal contact.
- 46. The method of claim 45, wherein the tungstencontaining compound comprises TDMAT, TDEAT, TiCl<sub>4</sub>, or combinations thereof.
- 47. The method of claim 45, wherein the reducing compound is selected from a group consisting of SiH<sub>4</sub>, B<sub>2</sub>H<sub>6</sub>, NH<sub>3</sub>, and combinations thereof.

48. The method of claim 45, wherein the adhesion layer is deposited within a first processing chamber and the barrier layer is deposited within a second processing chamber.

49. The method of claim 48, wherein the copper is deposited in a third processing chamber and the first, second and third processing chambers are each disposed about a common mainframe.